

# PATENT SPECIFICATION (11) 1 526 361

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- (21) Application No. 23677/76 (22) Filed 8 Jun. 1976 (19)  
 (31) Convention Application No. 7548038 (32) Filed 10 Jun. 1975 in  
 (33) France (FR)  
 (44) Complete Specification Published 27 Sep. 1978  
 (51) INT CL<sup>2</sup> C08K 9/10  
 (C08K 9/10 3/00 9/04)



- (52) Index at Acceptance  
 C3B 1C22 1C23 1C33A 1C5A 1C5B1 1C6B  
 1C6X 1C8P 1C8R 1D1B 1D2B 1D3  
 1L1B 1L2C1 1L3A 1L3B 1L4C 1L5A L  
 C1A K8  
 C3L DC  
 C3R 22C 3C 3N1 C22 C23 C33A C5A  
 C5B1 C6B C6X C8B L1B L2C1 L3A  
 L3B L4C L5A

- (72) Inventors: Jacqueline Cerny  
 Gilbert Vivant

## (54) COMPOSITIONS FOR FLAMEPROOFING PLASTICS

- 5 (71) We, RHONE-POULENC INDUSTRIES, a French Body Corporate of 22, 5  
 Avenue Montaigne, Paris 8<sup>eme</sup>, France, do hereby declare the invention for which we pray  
 that a patent may be granted to us, and the method by which it is to be performed, to be  
 particularly described in and by the following statement:-  
 10 The present invention relates to compositions, based on red phosphorus, for flamep-  
 roofing plastics. 10  
 Red phosphorus, in addition to various applications such as a coating for a match-striking  
 agent, has been used as a flameproofing agent for plastics. However, this application is

## ERRATUM

SPECIFICATION NO 1526361

Page 1, Heading (31) Convention Application No. for 7548038 read 7518038

THE PATENT OFFICE  
 13 March 1979

Bas 53513/7

- phosphine, which is very toxic and ignites spontaneously in air, especially at the tempera-  
 30 tures at which polymers are processed. 30  
 British Patent Specification No. 1.435.446 describes thermoplastics compositions flamep-  
 roofed by red phosphorus and containing metal oxides to prevent any evolution of phos-  
 phine during storage at ambient temperature. However, the addition of metal oxides is  
 insufficient to prevent the evolution of phosphine which occurs at high temperatures.  
 35 It is thus necessary to find a way of making it possible to employ red phosphorus without 35  
 the risk of phosphine evolution essentially due to the temperature which has to be used and  
 to the almost inevitable presence of small amounts of water in the polymers being moulded.  
 It has now been found, according to the present invention, that this latter object can be  
 40 achieved if compositions intended for flameproofing plastics are used which are in the form 40  
 of a powder or granules and comprise a mixture comprising:

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 particularly described in and by the following statement:-  
 10 The present invention relates to compositions, based on red phosphorus, for flamep- 10  
 roofing plastics.  
 Red phosphorus, in addition to various applications such as a coating for a match-striking  
 surface is also used as a flameproofing agent for plastics. However, this application is  
 restricted by the dangers encountered, such as pollution hazards, and difficulties in using the  
 material with complete safety. Red phosphorus is a very good flameproofing agent because,  
 15 for a given activity, it can be used in much smaller amounts than, for example, the halogen 15  
 derivatives. Furthermore, its use in plastics results in better mechanical properties and it  
 does not interfere with the electrical properties of the plastics.  
 It is already known, from French Patent No. 2,052,784, to use red phosphorus, in an  
 amount from 0.5 to 15%, as a flameproofing agent for moulding compositions based on  
 20 glass fibre-filled polyamides. However, red phosphorus used by itself directly in plastic 20  
 moulding compositions suffers from the disadvantage that its particles present the hazard of  
 igniting easily, for example in the presence of hot surfaces or under pressure.  
 To deal with these disadvantages, it has been proposed, according to British Patent  
 25 Specification No. 1,326,929 to incorporate into the thermoplastic material, which may be 25  
 reinforced with glass fibres, red phosphorus impregnated with a lactam containing 4 to 12  
 carbon atoms, for example caprolactam, in an amount from 1 to 20% based on the weight  
 of the polymer. The essential disadvantage of this process is the hygroscopic nature of the  
 lactams and the fact that the presence of water in the mixture causes the formation of  
 30 phosphine, which is very toxic and ignites spontaneously in air, especially at the tempera- 30  
 tures at which polymers are processed.  
 British Patent Specification No. 1,435,446 describes thermoplastics compositions flamep-  
 roofed by red phosphorus and containing metal oxides to prevent any evolution of phos-  
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 35 It is thus necessary to find a way of making it possible to employ red phosphorus without 35  
 the risk of phosphine evolution essentially due to the temperature which has to be used and  
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 It has now been found, according to the present invention, that this latter object can be  
 achieved if compositions intended for flameproofing plastics are used which are in the form  
 40 of a powder or granules and comprise a mixture comprising: 40

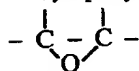
a) from 50 to 95% by weight of red phosphorus in the form of powder having a mean particle size not exceeding  $200\mu$  and

b) from 5 to 50% by weight of one or more epoxy resins.

"Red phosphorus", as used herein, is intended to cover all the coloured allotropic varieties which are sold commercially under the name red phosphorus and which can contain up to, say 3% of metal oxides or metal salts as stabilisers.

This red phosphorus must be in the form of particles having a mean diameter not exceeding  $200\mu$ , preferably not exceeding  $100\mu$ . The use of particles which are only a few microns in diameter makes it possible to flameproof spun articles for textile usage.

By epoxy resins, as used herein, are meant compounds containing more than one

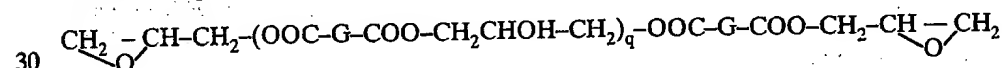


group, the compounds being present, depending on the proportion and nature of the starting reactants, either in noncrosslinked form in the form of a more or less viscous liquid or of a solid of relatively low melting point or in the form of a partially crosslinked product.

Essentially all the customary epoxy resins can be used in the compositions according to the invention. Thus it is possible to use polyglycidyl esters which can be obtained by reaction of a polycarboxylic acid with epichlorohydrin, or the dichlorohydrin of glycerol in the presence of an alkali. Such polyglycidyl esters can be derived from aliphatic dicarboxylic acids, for example oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid or dimerised or trimerised linoleic acid, and from aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, diphenyl-2,2'-dicarboxylic acid and the bis-(4-carboxyphenyl)

ether of ethylene glycol.

More specifically, such polyglycidyl esters include diglycidyl adipate and diglycidyl esters which correspond to the average formula:



in which G represents a divalent hydrocarbon radical, such as a phenylene group, and q represents an integral or fractional positive number.

Other examples of epoxy resins are the polyglycidyl ethers which can be obtained by interaction of a divalent or polyvalent alcohol and epichlorohydrin or a similar substance, for example the dichlorohydrin of glycerol, under alkaline conditions, or in the presence of an acid catalyst with subsequent treatment with an alkali.

These compounds can be derived from diols or polyols such as ethylene glycol, diethylene glycol, triethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, the polyhydroxylic cycloalkanes, hexane-2,4,6-triol, glycerol or the N-aryl-dialkanolamines, such as N-phenyl-diethanolamine, and are preferably derived from divalent or polyvalent phenols, such as resorcinol, catechol, hydroquinone, 1,4-dihydroxy-naphthalene, 1,5-dihydroxynaphthalene, bis-(4-hydroxyphenyl)-methane, 1,1,2,2-tetrahydroxyphenyl-ethane, bis-(4-hydroxyphenyl)-methyl-phenyl-methane, the bis-(4-hydroxyphenyl)-tolylmethanes, 4,4'-dihydroxydiphenyl, bis-(4-hydroxyphenyl)-sulphone and, in particular, 2,2-bis-(4-hydroxyphenyl)-propane or the condensation products of a phenol with an aldehyde.

Similarly it is also possible to employ aminopolyepoxides such as those which are obtained, for example, by dehydrohalogenation of the reaction products of epihalogenohydrins with primary or di-secondary amines, such as aniline, n-butylamine, bis-(4-aminophenyl)-methane or bis-(4-methylaminophenyl)-methane and the epoxy resins obtained by epoxidation of cyclic polyolefines such as vinylcyclohexane dioxide, limonene dioxide and dicyclopentadiene dioxide, the glycidyl ether of 3,4-epoxy - dihydro - dicyclo - pentadienyl, 3,4-epoxy cyclohexylmethyl 3',4' - epoxy - cyclohexanecarboxylate and its 6,6'-dimethyl derivative, ethylene glycol bis-(3,4-epoxy-cyclohexane)-carboxylate, the acetal formed between the aldehyde of 3,4-epoxy - cyclohexane and 1,1 - bis - (hydroxymethyl) - 3,4 - epoxy - cyclohexane, and epoxidised polybutadienes or epoxidised copolymers of butadiene with ethylenic compounds such as styrene and vinyl acetate.

Numerous works refer to the preparation of such epoxy resins, such as "The Encyclopedia of Polymer Science and Technology", Volume 6, page 209 et seq., Interscience Publishers, 1967.

The epoxy equivalent weight - which represents the weight of resin (in grams) which contains one gram equivalent of epoxy (groups) - can vary within very wide limits. Preferably, resins of which the epoxy equivalent weight is from 80 to 1,000 are used. As regards the physical characteristics of the resin, they range from liquid resins of very low viscosity,

for example 2 cPo at 25°C, to solids of which the melting point may be as high as, say, 180°C.

If it is desired to use the epoxy resin in the form of a crosslinked product, hot or cold curing agents of the usual types such as polycarboxylic anhydrides, or primary, secondary or tertiary, aliphatic or aromatic, amines, can be used. Such curing agents are described in "Encyclopedia of Polymer Science".

Depending on their physical form, the epoxy resins can, if they are liquid, be deposited on the surface of the phosphorus particles by any known means or, if they are solid, be mixed intimately, in the form of a powder, (with the phosphorus particles) by any known method of homogenisation of powders.

It is known that the addition of metal oxides or metal salts stabilises red phosphorus; the red phosphorus sold commercially usually contains these. Metal oxides, which make it possible to reduce possible evolution of phosphine, may be included in the compositions. The metal oxides which generally give the best results are the oxides of copper, zinc, silver, iron, antimony, vanadium, tin, titanium or magnesium; preferably copper oxide is used.

The amounts of metal oxides used can vary depending on the amount of epoxy resin used, depending on the conditions of use of the synthetic resins as well as on the nature of these synthetic resins. Usually, up to 100% by weight, based on the weight of the red phosphorus, of metal oxide can be employed.

Very many synthetic polymers can be used to obtain shaped articles which more and more frequently must be flameproofed. Numerous compositions based on thermoplastic polymers, thermosetting polymers or elastomeric polymers can be flameproofed according to the invention. Amongst the thermoplastic polymers there may be mentioned the polyolefines, such as high or low density polyethylenes, polypropylene, polyfluoroethylenes and ethylene-propylene copolymers, the polyvinyl compounds such as polyvinyl chloride or copolymers of vinyl chloride, the polystyrenes and acrylonitrile-butadiene-styrene copolymers, the polyamides such as poly(hexamethylene adipamide), polycaprolactam, poly(hexamethylene sebacamide), polyundecanamide, poly-lauryllactam and poly(hexamethylene azelamide), the saturated polyesters, such as poly(ethylene glycol terephthalates) or poly(butylene glycol terephthalates), the polycarbonates, the polyacetals and the polyacrylic compounds such as poly(methyl methacrylate), and the cellulose esters, polyurethanes or polyamide-imides.

Amongst the thermosetting polymers there may be mentioned the phenolic resins, the aminoplasts, the unsaturated polyesters, the polyepoxides and the polyimides.

Various elastomers can also be flameproofed using the compositions according to the invention, for example, the natural or synthetic rubbers, the silicones and the polyurethane elastomers.

All these plastics, especially when intended for producing shaped articles, are usually employed with various adjuvants, such as reinforcing fillers such as glass fibres, fillers intended to impart specific characteristics to the shaped articles or inert fillers such as kaolin or talc, antioxidants, various stabilisers, dyestuffs or pigments. 2 to 20% by weight of flameproofing composition relative to the plastics material is usually chosen to obtain a suitable flameproof effect. If the plastics composition is to contain a metal oxide of the type indicated hereinbefore, the metal oxide may be introduced in a composition together with the red phosphorus or as a separate component.

The following Examples further illustrate the present invention.

#### Example 1

35.7 g of an epoxy resin of the NOVOLAC type, having an epoxy equivalent weight of 180, are dissolved in 70 g of the dimethyl ether of diethylene glycol, also referred to as diglyme. 68.7 g of red phosphorus, as a powder having a particle size of between 20 and 30  $\mu$ , are suspended whilst stirring. The mixture is stirred for 5 minutes to give a homogeneous suspension and a solution containing 10.1 g of diaminodiphenylmethane and 20 g of diglyme is added. The batch is heated to 170°C for 2 hours, with constant stirring. Gelling takes place.

This gel is poured into a vessel containing 2 l of water and equipped with a turbine (stirrer). 112 g of a powder are obtained; this is isolated and dried.

30 g of the coated red phosphorus and 300 g of poly-(hexamethylene adipamide), having a mean molecular weight of 20,000 and an inherent viscosity, in meta-cresol, of 1.3, are introduced into a jacketed one litre autoclave equipped with a spiral scraper-type stirrer revolving at 20 rpm and heated by heating fluid. The mixture is heated gradually, whilst stirring, so that it reaches a temperature of 285°C after one hour. It is maintained at this temperature for one hour.

Any phosphine which may be evolved is determined. To do this, the gases, on leaving the autoclave, are trapped in two 1,000 cm<sup>3</sup> flasks in series, containing 750 cm<sup>3</sup> of a 2, strength

aqueous solution of mercuric chloride, and the acid formed is determined in the presence of methyl orange.

This method of determination has been described by Mr. WILMET in "Comptes rendus de l'Academie des Sciences" 185 (1927), page 206.

5 The weight of phosphine evolved is 7 mg per 1 g of red phosphorus employed. 5

A blank experiment carried out under the same conditions but with 18 g of red phosphorus in the absence of epoxy resin gives an evolution of phosphine of 33.5 mg per gram of red phosphorus employed.

10 To test the flameproofing produced by the red phosphorus and the epoxy resin, plates of size 100 mm × 6 mm, and of 3 mm thickness, are prepared by cold sintering under a pressure of 300 kg/cm<sup>2</sup>. 10

The limiting oxygen index is measured by the LOI test in accordance with Standard Specification ASTM D 2863.

15 The following results are obtained: 15

	LOI test
Polymide alone	20.8
Ployamide + red phosphorus	26 - 27

20 *Example 2* 20

The procedure of Example 1 is followed, but 6 g of copper oxide are added to the red phosphorus coated with epoxy resin.

No evolution whatsoever of phosphine is observed.

25 *Example 3* 25

An epoxy resin powder is prepared by following the procedure indicated in Example 1, but without adding red phosphorus.

Thereafter, 12 g of epoxy resin powder and 18 g of red phosphorus powder are mixed.

30 The mixture is then introduced into the autoclave with 300 g of polyamide, and the procedure indicated in Example 1 is followed. 30

11 mg of phosphine are evolved per gram of red phosphorus employed.

*Example 4*

35 A single-screw laboratory extruder of which the screw has a length of 415 mm and a diameter of 15 mm is used. This extruder is equipped with a cylindrical die having a diameter of 3 mm. The barrel temperatures are as follows: 250°C at the material inlet, 280°C at the centre and 270°C at the die. 35

40 The following composition is prepared by simple mixing: 100 g of poly(hexamethylene adipamide) having a mean molecular weight of 20,000 and an inherent viscosity, in meta-cresol, of 1.3, 20 g of red phosphorus coated in accordance with Example 1 and 4 g of copper oxide powder. 40

This composition is introduced into the extruder and a strand is extruded.

45 During the entire operation, the possible presence of phosphine in various parts of the extruder is tested for by means of a DRAEGER [Registered Trade Mark] CH 31,101 tube. Equally, attempts are made to detect phosphine when the strand which has just been extruded, and which is still hot, is broken. 45

All these tests are negative.

*Example 5*

50 The coated red phosphorus is prepared as follows: 50

120 g of red phosphorus powder are mixed with 65.3 g of epoxy resin having an epoxy equivalent weight of 845 (melting point = 90–100°C) and 14.7 g of melamine by agitation in a revolving drum. The mixture thus obtained is deposited at a thickness of about 1 cm on a plate and is heated in an oven for 3 hours at 120°C and then for 3 hours at 150°C. The slab obtained after cooling is ground to give granules. 55

55 The following composition is prepared by simple mixing: 87.7 g of poly(tetramethylene glycol terephthalate) granules (viscosity 3,500 poises), 0.3 g of cepretol (polyalkylene glycol laurate), 2 g of copper oxide powder and 10 g of coated red phosphorus.

60 This composition is introduced into the extruder used for Example 4 and is extruded as strands. The barrel temperatures are as follows: 215°C at the material inlet, 240°C at the centre and 235°C at the die. No evolution of phosphine is detected in any area whatsoever. 60

*Example 6*

65 The procedure of Example 5 is followed, replacing the poly(tetramethylene glycol terephthalate) by the same amount of polypropylene powder having the following charac- 65

teristics:  $d = 0.903$ , melting point:  $165 - 170^{\circ}\text{C}$ , melt index: 6 (at  $230^{\circ}\text{C}$  under 2.16 kg, in g/10 minutes).

The temperatures are respectively  $205^{\circ}\text{C}$ ,  $220^{\circ}\text{C}$  and  $205^{\circ}\text{C}$ . No evolution whatsoever of phosphine is detected.

#### Example 7

The procedure of Example 5 is followed, replacing the poly(tetramethylene glycol terephthalate) by the same amount of polystyrene powder,  $d = 1.05$ , melt index 4 - 4.5 (at  $200^{\circ}$  under 5 kg). The extruder temperatures are, respectively,  $220^{\circ}\text{C}$ ,  $240^{\circ}\text{C}$  and  $230^{\circ}\text{C}$ . No evolution whatsoever of phosphine is detected.

The limiting oxygen index is measured

	LOI test
Polystyrene alone	19
Polystyrene + phosphorus	22

#### Example 8

1,500 g of red phosphorus powder and 1,000 g of epoxy resin (epoxy equivalent weight 845, melting point  $90 - 100^{\circ}\text{C}$ ) are mixed by agitation on rollers. The powder mixture is spread on a plate to a thickness of about 1 cm and is then heated in an oven at  $130^{\circ}\text{C}$  for 3 hours. After cooling, it is cut into humbug-shaped pieces. The granules contain 60% of red phosphorus.

Poly(hexamethylene adipamide) (molecular weight 20,000) filled with 30% of glass fibres is flameproofed. The following ingredients are mixed: 88.7 g of filled polyamide, 0.3 g of cepretol, 1 g of copper oxide and 10 g of coated red phosphorus.

An extruder (described in Example 3) is fed with this mixture. The barrel temperatures are:  $265^{\circ}\text{C}$  at the material inlet,  $280^{\circ}\text{C}$  at the centre and  $265^{\circ}\text{C}$  at the die.

A strand of good quality is obtained, without detecting phosphine in any part of the extruder.

#### Examples 9 to 11

The following polymers described in Examples 5 to 7, are flameproofed by means of the coated red phosphorus prepared according to Example 8: poly(tetramethylene terephthalate), polypropylene and polystyrene.

The working conditions and the amounts are the same as those described in Examples 5 to 7.

In all these experiments, a strand of good quality is obtained and no evolution whatsoever of phosphine is detected by means of the DRAEGER CH 31,101 tube.

Attention is drawn to the related application No. 23679/76 (Serial No. 1526363) which describes and claims a plastics composition which contains from 0.1 to 20% by weight, based on the weight of the plastics material, of red phosphorus in the form of particles having a mean diameter not exceeding  $200\mu$ , encapsulated in a polymer which does not melt or soften below  $90^{\circ}\text{C}$  and which has a mean molecular weight of at least 2,000.

#### WHAT WE CLAIM IS:-

1. A flameproofing composition in the form of a powder or granules which comprises a mixture comprising

a) from 50 to 95% by weight of red phosphorus in the form of a powder having a mean particle size not exceeding  $200\mu$  and

b) from 5 to 50% by weight of one or more epoxy resins (as hereinbefore defined).

2. A composition according to claim 1 in which b) is a non-crosslinked epoxy resin.

3. A composition according to claim 2 in which the epoxy resin is a polyglycidyl ester or ether or an aminopolyepoxide.

4. A composition according to claim 1 in which b) is an epoxy resin crosslinked by means of a curing agent.

5. A composition according to any one of claims 1 to 4 in which the epoxy resin is a polymer having an epoxy equivalent weight of from 80 to 1,000.

6. A composition according to claim 1 in which the epoxy resin is one specifically identified herein.

7. A composition according to any one of claims 1 to 6, which also contains up to 100% by weight, based on the weight of the red phosphorus, of an oxide of copper, zinc, silver, iron, antimony, vanadium, tin, titanium or magnesium.

8. A composition according to claim 1 substantially as hereinbefore described.

9. A composition according to claim 1 substantially as described in any one of Examples 1 to 3, 5 and 8.

10. A plastics composition which comprises from 0.2 to 20% by weight based on the weight of the plastics material of a flameproofing composition as claimed in any one of the preceeding claims.
- 5 11. A composition according to claim 10 in which if the flameproofing composition is not one as claimed in claim 7 the composition contains up to 100% by weight based on the weight of the red phosphorus of a metal oxide as defined in claim 7. 5
12. A composition according to claim 10 or 11, which is filled with glass fibres.
13. A composition according to claim 10 or 11, filled with talc or kaolin.
- 10 14. A composition according to claim 10 substantially as hereinbefore described.
- 10 15. A composition according to claim 10 substantially as described in any one of Examples 1 to 11. 10

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1978.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

